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NATIONAL BUREAU OF STANDARDS

Technical News

BULLETIN

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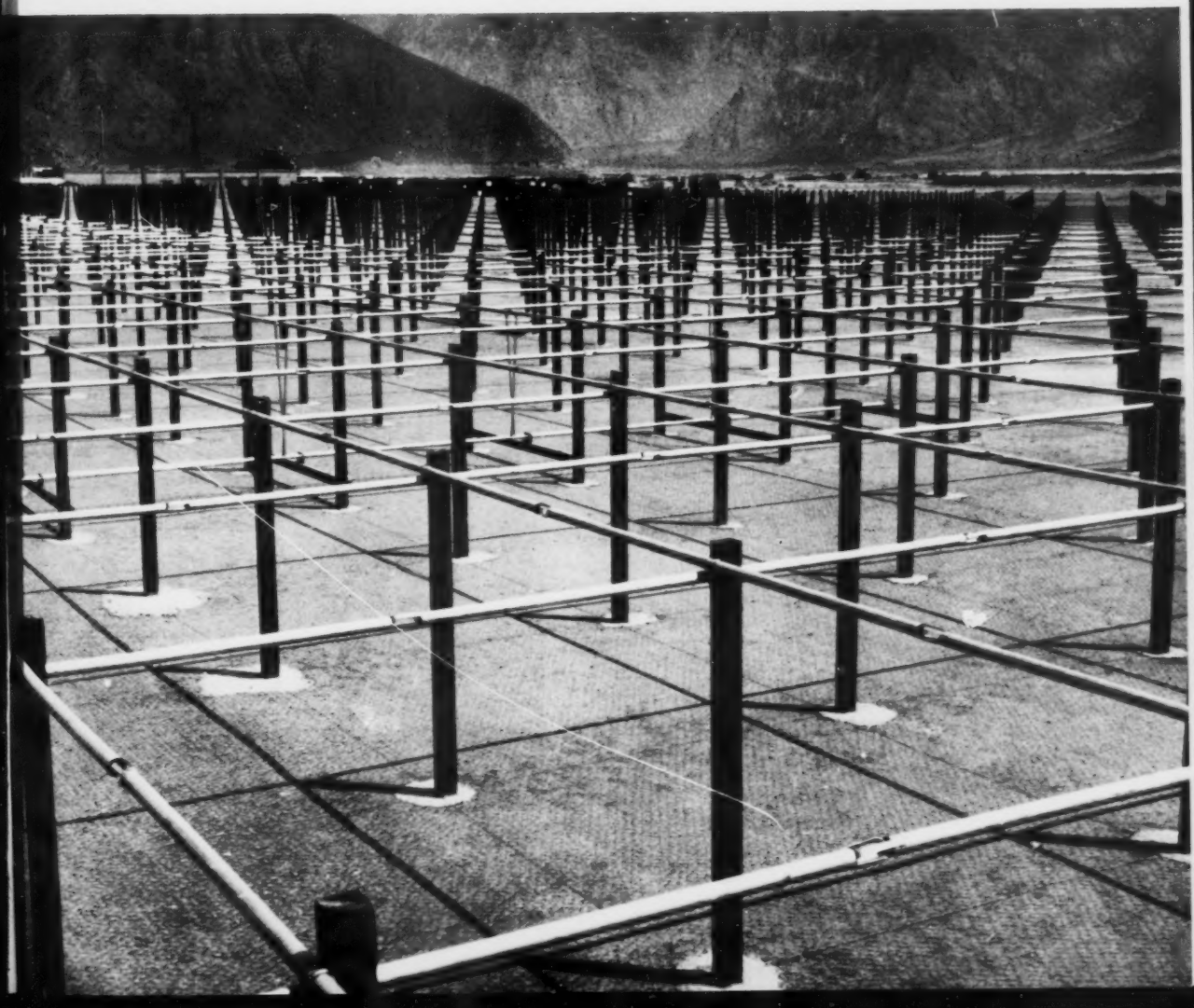

U.S. DEPARTMENT OF COMMERCE — LUTHER H. HODGES, *Secretary*

NATIONAL BUREAU OF STANDARDS — A. V. ASTIN, *Director*

NATIONAL BUREAU OF STANDARDS

Technical News

BULLETIN

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COVER: A portion of the 89,000 m² antenna being constructed by the National Bureau of Standards Boulder Laboratories and the Instituto Geofisico de Huancayo (Peru) near Lima, Peru. The antenna will be used in conjunction with a 6-Mw transmitter for ground-based radio exploration of space. (See "Scatter Radar Investigation of Upper Atmosphere and Outer Space," p. 163.)

Scatter Radar Investigation of Upper Atmosphere and Outer Space

AN INSTALLATION for ground-based explorations of the upper atmosphere and outer space is being constructed by the Bureau's Boulder (Colo.) Laboratories and the Instituto Geofisico de Huancayo (Peru) at a site 27 km east of Lima, Peru. The Jicamarca Observatory—named for a nearby village—will have, when completed, a 6-million-watt pulse transmitter and an 89,000 m^2 antenna with 9216 crossed dipoles mounted 1.8 m above a reflecting ground screen. The antenna will be used to transmit a very high frequency wave lasting from 50 to 1500 microseconds, and when switched to the receiving state, to detect the faint re-radiation of the pulsed radio wave by free electrons in the upper atmosphere.

Employing this scatter radar technique developed by K. L. Bowles of the Bureau's Central Radio Propagation Laboratory, the Observatory will be used in the measurement of: Electron densities at heights from 100–3000 km; the kinetic temperature of the ions, 200–3000 km; the percentage composition of major ionic components, 200–700 km and 1200–1800 km; and the intensity of the earth's magnetic field. It will also be used in limited observations of radar echoes from the sun's corona and from solar gas clouds emitted by solar disturbances, in studies of small-scale irregularities in the outer atmosphere, and in studies of the *D*-region of the ionosphere, particularly its turbulence and meteorology. Other applications include the calibration of satellite instrumentation, and searching for radio stars one magnitude weaker than those observed to date.

The Peruvian location was chosen for several reasons: In this area, the lines of force of the earth's magnetic field are nearly horizontal, a condition which should make it possible to conduct analyses of the chemical composition of the ionosphere and other related experiments that cannot be performed elsewhere. This spring saw the first rain since 1935; this lack of rainfall is an important factor in keeping the large antenna and its many elements in good working condition. Continuing 15 years of cooperation with the Bureau, the Instituto Geofisico de Huancayo prepared the way for this major construction effort, and is assisting in the work. The Peruvian government provided the land, permitted customs-free import of the necessary equipment, and has insured a clear airspace overhead.

The antenna, consisting of crossed-dipole elements mounted 1.8 m above a ground reflecting screen, is about half completed. Using generators of less than the expected peak power, measurements of electron densities have been made to altitudes of 1200 km. The full 6-Mw transmitter is expected to be operational in December 1961.

Artist's concept of the scatter-radar technique by which the Jicamarca Observatory will study the upper atmosphere. Pulses from the broadside antenna are re-radiated by free electrons in the upper atmosphere and detected by the antenna system.

Members of the Jicamarca Observatory staff discuss plans for the construction of the site. Shown here are (left to right): J. L. Green and K. L. Bowles, NBS, Max Tabara, Instituto Geofisico de Huancayo, G. R. Ochs and G. F. Miller, NBS, and Antonio Arevalo, Instituto Geofisico.

Redetermination of NBS Unit of Resistance by New Method

THE PRIMARY UNIT of electrical resistance maintained by the Bureau has been redetermined by a new, more accurate method. The evaluation [1] is based on a nominally 1-pf capacitor, the value of which may be calculated to a high degree of accuracy from its mechanical dimensions.

Measurements made by a group under the direction of R. D. Cutkosky using the new method indicate that the NBS unit of resistance is 1.000002_3 ohms with an estimated 50 percent error of 2.1 ppm (parts per million) based on the statistical uncertainty of the measurements and allowing for known sources of possible systematic errors other than in the speed of light, assuming that the speed of light is 2.997925×10^{10} cm/sec.

Because of the need in modern science and industry for precise electrical measurements, the Bureau permanently maintains the basic primary standards of voltage and resistance from which other electrical quantities are derived. The national standard of resistance is maintained with a group of 1-ohm manganin resistors. The values assigned to these resistors are calculated from extremely precise measurements made in terms of the basic mechanical units of length and time. Such measurements, which must be periodically repeated, serve to fix the relation between the electrical and mechanical units.

The most accurate methods for performing these evaluations previously have made use of either self inductors or mutual inductors having inductances computable from their mechanical dimensions. In principle, it is a straightforward procedure to compare the impedance of the computable inductor at a known frequency with that of the 1-ohm reference standard resistors. In practice, this comparison is likely to involve several steps and the currents through the inductor may not be sinusoidal, so that the impedance concept becomes somewhat ambiguous.

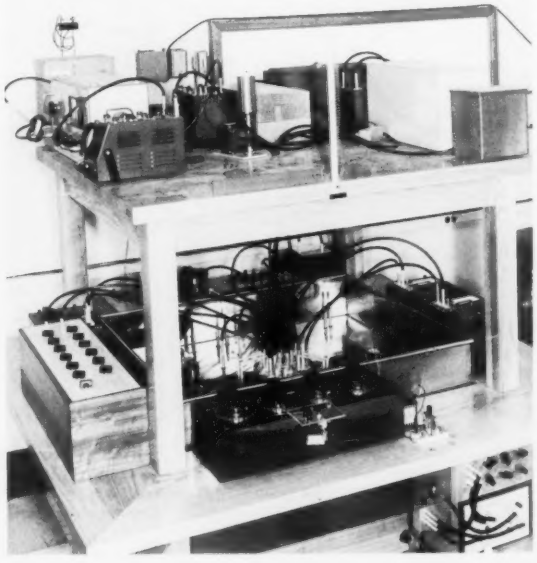
An alternative method for assigning values to the reference resistors involves the construction of a capacitor such that its capacitance may be calculated from its mechanical dimensions. The impedance of the capacitor at a known frequency can then be compared with that of the reference standard resistors to establish the values of the reference resistors in terms of the prototype standards. In addition to increased accuracy, this method has the advantages of speed and simplicity in both the measurements and the construction of the equipment required to make them.

Evaluation of computable capacitors of most types requires the measurement of several dimensions to a higher accuracy than is required of the capacitance being computed. The development by D. G. Lampard and A. M. Thompson [2] of a device called a computable cross capacitor has made possible the construction of a capacitor having a value computable from dimensional measurements with an accuracy considerably higher than that attainable with any previous design.

The version of a cross capacitor developed by the Bureau is constructed of gage blocks. Its capacitance

J. Q. Shields assembles the gage blocks used to form the computable cross capacitor.

Frequency-dependent bridge used with the computable cross capacitor in the recent evaluation of the NBS unit of electrical resistance.



is computable in electrostatic units from the known lengths of two of the gage blocks. Conversion to electromagnetic units requires an accurate value for the speed of light.

This cross capacitor was used recently in an evaluation of the NBS unit of resistance. The measurements involved an impedance step-up by a factor of 10^4; for this purpose a new type of frequency-dependent bridge was employed which allows the use of completely shielded, three-terminal components.

The close agreement between the value of the NBS unit of resistance obtained using the computable capacitor with the value as determined directly in electromagnetic units by the older methods involving computable inductors demonstrates that the two approaches, one involving the speed of light, are consistent to within a few parts per million. This agreement also implies that the presently accepted value for the speed of light is not grossly in error.

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[1] *For further information, see* An evaluation of the NBS unit of resistance based on a computable capacitor, *J. Research NBS* **65A** *(Phys. & Chem.) No. 3, 147 (1961).*

[2] A new theorem in electrostatics and its application to calculable standards of capacitance, *by A. M. Thompson and D. G. Lampard, Nature* **177,** *888 (1956).*

Photoelectric Pyrometer Developed

A PYROMETER which utilizes a photoelectric system rather than the human eye for detecting radiance matches has been developed.[1] This instrument has a precision at 1063 °C of 0.02 deg C, as compared to a precision of about 0.3 deg C for the NBS visual optical pyrometer at the same temperature. After stability testing and calibration, the photoelectric pyrometer is expected to provide an improvement of an order of magnitude in the realization of the International Practical Temperature Scale above 1063 °C. Potential applications of this device include calibration of optical pyrometers and tungsten-strip lamps, and redetermination of the platinum point.

In general, an optical pyrometer consists of an optical system through which an observer views the object whose temperature is being determined, and a power supply which is used to apply an adjustable current to a thin tungsten filament of a pyrometer lamp within the optical system. The current is adjusted until, in the observer's judgement, the filament disappears in the background image of the object being viewed. Brightness temperature determinations made with an optical pyrometer depend upon the sensitivity of the human eye to differences in brightness, and upon knowledge of the mean effective wavelength of the radiation being viewed. Psychological factors in judgment may also be involved. By use of photoelectric means of detection, these limitations may be substantially reduced.

The optical system of the photoelectric pyrometer differs from that of a conventional pyrometer in that images of both the source and the pyrometer lamp are focused in a plane containing a slit rather than in the focal plane of an ocular. The surface containing the slit has been highly polished, so that a reflected image is available for visual alinement of the pyrometer. Radiation passing through the slit falls on a photomultiplier tube, the amplified output from which is recorded on a strip chart. The images of the source and the pyrometer lamp are alternately positioned on the slit, and the phototube response, as seen on the strip chart, guides the operator in making adjustments in the pyrometer lamp current. A multielement filter in the optical system isolates a band of wavelengths at 6530 A having a half-width of about 110 A. This bandwidth is about one-fifth of that in visual optical pyrometry, and should permit the determination of the mean effective wavelength with greater accuracy.

The long-term stability of the pyrometer is now being investigated. Three pyrometer lamps are incorporated in the pyrometer, and can be interchanged for making radiance matches. Despite extensive heat treatment of the lamps prior to their use in the pyrometer, unexpected gradual changes up to 0.5 deg C in 150 hrs have been detected. Work is being continued to improve the stability of these lamps.

Possible inaccuracies of from 0.1 to 0.2 deg C, resulting from differences in the size of the source, have been uncovered during the testing of the pyrometer. Fortunately, a simple procedure is available for determining differences in the size of the source being observed and that used in the primary calibration. This is done by momentarily blocking off the source while the image of the pyrometer lamp filament is focused on the slit. The magnitude of the resultant decrease in phototube response is used as a measure of the size of the source.

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[1] *For further details, see* The NBS photoelectric pyrometer of 1961, *by R. D. Lee, to appear in vol. 3, Temperature, its measurement and control in science and industry, Reinhold Pub. Co. (to be published).*

Photoelectric pyrometer detects radiance matches with a photoelectric system rather than the human eye. An order of magnitude improvement in the realization of the International Practical Temperature Scale above 1063 °C is expected through use of this instrument. R. D. Lee adjusts the pyrometer during measurements of a strip-lamp source.

Millimeter Wave Fabry-Perot Interferometer

BY TREATING very short radio waves as light waves, William Culshaw of the Bureau's Boulder (Colo.) Laboratories has developed a technique for probing millimeter waves—a largely inaccessible region of the radio spectrum. The basic development, a reflector to resonate these waves [1], can be used with associated equipment to determine the length of millimeter waves, or to investigate various materials when exposed to these waves.

Radio waves are normally resonated in a metal box. The box is built to precise dimensions, depending upon the wavelength involved, to achieve maximum resonance at different frequencies. The NBS device, however, differs from previous resonators in that it has two perforated ends and no sides. The ends look like two small squares of pegboard except that they are made of polished brass or silver.

In the radio spectrum, millimeter waves form a band of frequencies between microwaves and the infrared. Millimeter waves are a rich field for research in that they are best suited for studying molecules and atoms which resonate at similar frequencies (100 thousand million vibrations per second). They can be used for studying the properties of superconducting materials and for studying the electron density of heavily ionized gases. Also, a better understanding of these frequencies will probably lead to new devices just as radar developed from the ability to handle microwaves.

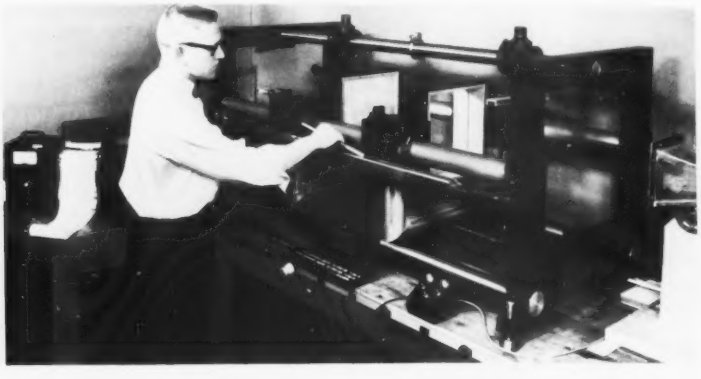
The short length of millimeter waves, which makes them important to research and development, also makes these waves very hard to handle. Previously, there had been no efficient way either to generate or to resonate radio waves which are this short.

The length of a normal cavity resonator is about one-half of the wavelength being studied. This means that it is very difficult to build a cavity with the necessary precision for millimeter wavelengths because its surface irregularities must be only a small fraction of a wavelength and therefore they must be no larger than a few millionths of a centimeter. However, when a resonant cavity is used to study electrons, atoms, or molecules, the cavity must be big enough to allow sufficient interaction between them and the electric field inside the cavity. Until now such studies have been impossible at millimeter wavelengths, for the normal cavities are too small.

By treating millimeter waves as light waves, responses or "fringes" resulting from the interference of wave trains have been achieved that are more than ten times sharper than those achieved in the fields of either radio or optics. The cavity resonator developed at the Bureau consists of two perforated sheets of metal. The size of the sheets (normally 15 to 30 cm sq), and the size and spacing of the holes, are carefully calculated for the frequency involved. In one case the metal plates consisted of perforated sheets of brass 0.08 cm thick and 30 cm sq. The reflectivity of these plates was about 99.9 percent. Plates made of perforated films of silver deposited on glass have been used, and silver on quartz optical flats will also be tried. One of the plates is fixed but the other is movable, so that the spacing between the plates can be precisely adjusted.

The holes in these plates are simple in concept but they must be carefully designed and made. Electronically speaking, they act as perfect transformers to "couple" the millimeter waves into and out of the cavity while maintaining a high Q value inside the cavity. The effectiveness of the holes depends upon their diameter and spacing, and these dimensions vary with the frequency. In an interferometer for 6-mm wavelengths, which uses perforated silver films, these holes are 0.60 m in diameter and they are spaced 1.45 mm between centers.

The two plates are placed parallel to each other and millimeter waves are beamed against the fixed end of this "box". Because the holes are so small, only a tiny fraction of the initial energy passes through the holes in the fixed plate. This energy strikes and is reflected by the second plate, with only a tiny fraction passing through it. As the polished metal surfaces are highly reflective, the waves that are "captured" inside the cavity are reflected back and forth and, when the plates are properly spaced, the cavity resonates. When the spacing between the plates is correct the transmission through the cavity is a maximum. Inside the



M. V. Anderson uses a precision end gage to measure the spacing between the two plates of the 6.28-mm Fabry-Perot interferometer. The transmitting horn is at extreme right; a portion of the receiving horn is visible at far end of instrument. Fringes produced by the instrument are recorded on strip chart at left. This device has been used to measure the length of millimeter waves to an accuracy of 0.04 percent.

cavity this condition creates an entire series of "standing" waves—one between each pair of holes at either end of the unit.

The perforated plates control millimeter waves much as semiopaque mirrors control light waves. Present plates are flat to tenths of thousandths of a centimeter and thus the waves tend to be reflected back and forth (at the spacings used) with almost no loss of energy through the open sides of the cavity. Also, because there are no sides, the size of the cavity is adjustable over a wide range of frequencies; as the cavity is large in comparison with the wavelength, it is much more precise and is easier to use than a conventional cavity.

To make the cavity resonate, the adjustable plate is slipped (on steel mounts) slowly away from the fixed plate. Maximum resonance (and output) occurs each time the distance between the plates is increased by exactly one-half wavelength. The plates are normally operated about 15 cm apart but are effective (depending upon their size and frequency) at spacings up to about 1 m. An important value of these cavities is that the signal strength goes through very sharp maximums at each half-wavelength spacing. For this reason these spacings can be measured with great precision.

This type of cavity has been carefully tested by using it as the resonant cavity for a millimeter wave Fabry-Perot interferometer—an instrument whose basic design was originally developed for light waves. The interferometer provides a transmitting "horn" with plastic lenses to send millimeter waves into the cavity, a receiving horn to pick up waves coming out of the cavity, and instrumentation to record variations in the output signal.

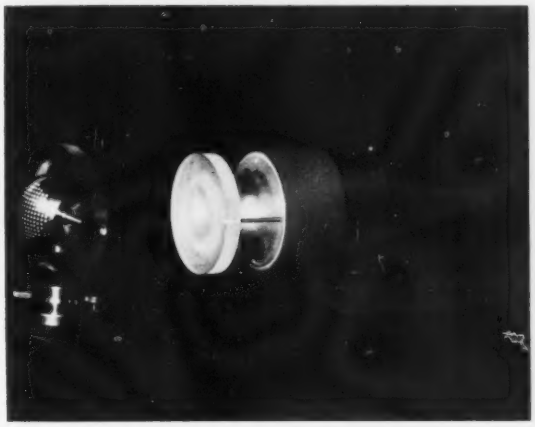
The interferometer has already been used to measure the wavelength of millimeter waves with accuracies of better than 0.04 percent. This method of wavelength measurement, for these short wavelengths, gives the sharpest fringe ever obtained with such an instrument (in radio or optics) and is more accurate than other available wavemeters. With further development it promises to give even higher accuracies.

Because of the cavity's ability to build up many reflections between the two plates—with almost no energy loss—its storage capacity is high. This means that its precision, or "*Q*" factor, is also extremely high. Until now this result has been very difficult to obtain at millimeter wavelengths. In tests of radio waves, which were about 6 mm long, the cavity attained *Q* values of around 100,000—10 to 50 times better than the theoretical *Q* values which could be obtained by a normal cavity.

In addition to providing a relatively large, workable device for resonating millimeter waves, such cavities can also be used in relatively high-powered generators since they can build up a millimeter signal from electron streams. Also, they become even more efficient at shorter wavelengths and are thus a practical and efficient tool for exploring the millimeter and submillimeter wave regions.

The cavities are relatively simple and easy to make and are not limited in shape. For example, a spherical (bi-conical) cavity, made of gold-plated silver, and

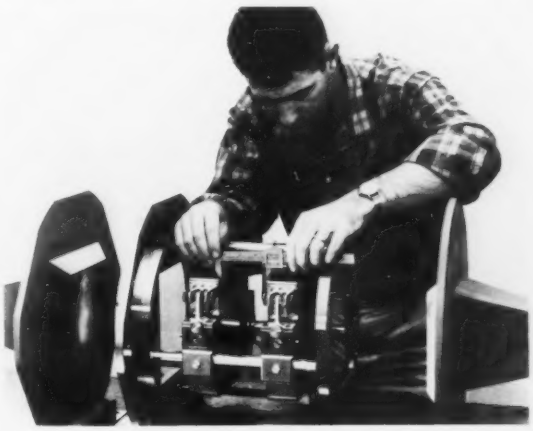
Bi-conical, spherical cavity illustrates design flexibility of the perforated cavities. Millimeter waves are beamed by the horn (right) through two plastic lenses which focus the waves on the cavity (left). In actual operation the two lenses are recessed into the horn.



with two sides of the sphere perforated with holes, has been operated by focusing energy to the center of the sphere. The first sphere, primarily designed to test the spherical concept, is 10 cm in diameter and operates successfully at a wavelength of 8 mm.

This type of perforated cavity should be particularly valuable for the electronic generation of power and for studies at millimeter and sub-millimeter wavelengths. It offers a possible solution to the problem of designing a resonator, at these wavelengths, for two- and three-level solid-state masers.

Although the cavities are designed to resonate at a particular frequency, they have enough bandwidth to permit operation over a wide range. This makes them applicable to the study of different materials and for use in masers.



Fabry-Perot interferometer, designed to operate at 3–4 mm, used as the cavity resonator for a hydrogen cyanide gaseous maser. G. L. Strine adjusts the parallelism of the perforated reflectors.

The 6-mm interferometer is being used to study various materials (such as plastics) by placing sheets of these materials in the center of the cavity—parallel to the plates themselves. Since the radio waves must now be reflected back and forth through the substance being studied, there is a change in the length of cavity required for resonance. The amount of this change is a measure of the material's dielectric constant.

Another Fabry-Perot millimeter wave interferometer (3.4-mm wavelength) is being used inside a maser. Initially, this device is being used to study molecule of hydrogen cyanide which resonate at this wavelengt The Bureau is also constructing a Michelson-type inter ferometer which will use millimeter waves to make a new determination of the speed of light.

[1] *For further technical details, see* Reflectors for a microwave Fabry-Perot interferometer, *by W. Culshaw, IRE Trans. on Microwave Theory and Techniques,* **MTT–7,** *221 (April 1959); see also* High resolution millimeter wave Fabry-Perot interferometer, *by W. Culshaw, ibid.,* **MTT–8,** *182 (March 1960).*

Improved Electron Filter Lens

AN ELECTRON FILTER LENS having improved characteristics has been designed and assembled at the Bureau. This design[1] has the advantages of longer focal length and increased aperture while maintaining an energy resolution, at 5 kev primary energy, of less than the thermionic spread of the initial beam.

An electron filter lens is an electrostatic lens so designed that electrons having energies above some critical value are transmitted while those with energies below this value are rejected. The critical value is associated with the potential of an electric potential barrier. In the past, filter lenses have been used for increasing the contrast of diffraction diagrams and electron micrographs [2, 3] by rejecting the inelastically scattered background; recently they have been used for ion-energy analysis.[4]

Filter lenses have been made in three general forms. The resulting performance, although satisfactory for purposes requiring a short-focus device, is unsuitable for other applications.

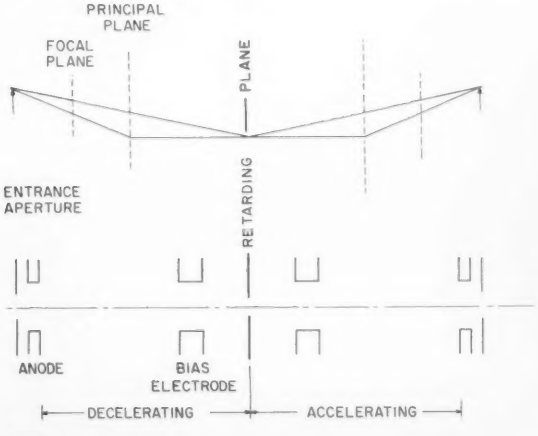
When J. A. Simpson and L. L. Marton recently needed a filter lens to be used as an electron monochromator, they found that the initial beam and the final filtered beam were required to be essentially collimated. A very long, preferably infinite, focal length was therefore desirable.

The reduction of the energy of the electrons in the plane containing the saddle point (the point of most negative potential in the path of the transmitted beam) leads to strongly curved paths, high angular divergences, and hence short focal lengths. Use of a classic lens for this purpose would have necessitated a second lens of short focus to recollimate the beam. However, such a procedure would have resulted in interference with the filter lens field by the electric or magnetic fields of the short-focus lens, which usually extend far beyond the lens' focal plane. A long-focus recollimating lens, while not causing this difficulty, would lead to undesirably large beam diameter.

The problem of recollimating the beam was solved by obtaining an intermediate image in the saddle plane. The large divergences in this plane thus have no effect on the final design.

The application of this principle of intermediate imaging is a filter lens consisting of two short-focus lenses symmetrically placed about the saddle plane. One lens forms a small image of the entrance aperture to this plane and retards the electrons to the saddle point. The second forms an image of the saddle plane at the exit aperture, and accelerates the electrons to their initial energy. The principle of operation of the

Schematic diagram of electron filter lens, showing path of electrons through lens elements.



J. A. Simpson adjusts the entrance aperture of the electron filter lens. Detector current is read on the microammeter in the foreground. Lens is being used as an electron energy analyzer in an inelastic scattering experiment. Background apparatus includes the electron source and scattering equipment, protected from interfering magnetic fields by Helmholtz coils.

filter lens is therefore that of two electron immersion lenses placed back to back.

The two stages of the filter lens can be designed using data concerning lenses employed in emission microscopy.[5, 6] Such data provided the Bureau with a starting point for the design of a series of lenses. Giving detailed attention to the most promising design resulted in a lens that can be used at energies up to 40 kev. In conjunction with a photomultiplier tube, it becomes a high-resolution electron analyzer.

Since earlier filter lenses were designed for specific applications, the importance of particular characteristics differs among them. Data on all these characteristics are therefore incomplete. In a comparison with the most complete set of data available on an earlier lens,[4] it can be seen that the new lens will tolerate much wider beams, or alternately, more misalinement, for equal sharpness of cutoff. A direct comparison of range cannot be made, as even the largest aperture of the new lens is satisfactory for as great a range as that for which comparison data are available.

The measured spatial resolution of the lens, when set 1 v from cutoff, is 50μ, which is sufficient for many purposes.

The output of the lens is a well-collimated beam, about 1 mm in diameter, which cuts off without significant change in size. Such an electrode configuration may therefore be useful as a beam-blanking element in high-speed cathode-ray tubes. In this application, the very low drive requirements and distance from the cathode are advantageous.

[1] *For further details, see* An improved electron filter lens, *by J. Arol Simpson and L. Marton, Rev. Sci. Inst.* **32**, *No. 7, 802 (1961).*

[2] *Boersch, H., Naturwiss.* **35**, *26 (1948); Optik* **5**, *436 (1949); Z. Physik* **139**, *115 (1951).*

[3] *Mollenstedt, G., and Rang, O., Z. Angew. Physik* **3**, *187 (1951).*

[4] *Forst, G., Z. Angew. Physik* **10**, *546 (1958).*

[5] *Septier, A., Compt. Rend.* **235**; *609, 652, 1671 (1952).*

[6] *Soa, E. A., Jenaer Jahrbuch 1959, Pt. 1, 115 (Carl Zeiss Jena, 1959).*

STANDARD MATERIALS

Standard Samples of Hydrogen-in-Titanium

Three new gas-in-metal standard samples[1]—of titanium containing three different levels of hydrogen—are now available. These reference materials, developed by J. T. Sterling and L. L. Wyman of the chemical metallurgy laboratory, are part of a series initiated in 1959 to provide standards of gases-in-metals for a variety of metallurgical products. Such standards are suitable for calibrating chemical analytical equipment employed to measure the gas content in various alloys. The first standard samples[2] of the series, eight bars of iron and low-carbon steels, are certified for their oxygen and nitrogen content.

Because the usefulness of titanium alloys increases as their gas content decreases, improved specifications limiting the amount of gases present are required for titanium alloys, especially those used in rockets and missiles. By calibrating analytical apparatus with standard samples, the gas content of such materials can be successfully monitored.

For preparing the reference standards, large sheets of commercially pure titanium are treated with hydrogen. Next, by controlled heating under vacuum, part of the hydrogen is extracted until the desired level of gas concentration is reached. The treated metal sheets are then divided into samples approximately 0.25 in. by 0.25 in. by 0.055 in.

To test the homogeneity of these sheets, random samples from different sections were analyzed. By using the hot-extraction technique, hydrogen in the metal can be completely recovered for analysis. For this operation, the sample was first washed in a volatile solvent to remove surface contaminants. It was then weighed and heated in a vacuum furnace at 1400 °C. The liberated hydrogen was collected for analysis. The hydrogen thus obtained was evaluated as molecular hydrogen. Ranges of acceptable values for the three hydrogen levels are 32, 98, and 215 ppm.

The standards may be purchased for $10.00 per sample from the Standard Sample Clerk, National Bureau of Standards, Washington 25, D.C. A certificate of analysis plus directions for preparation are distributed with each sample.

Work is now in progress to develop titanium standard samples with precisely determined contents of oxygen and nitrogen. After this study, standards for gases in uranium and zirconium will be prepared.

[1] *Standard samples issued by the Bureau are described in* Standard Materials, *NBS Circular 552 (third edition), which may be obtained for 35 cents from the Superintendent of Documents, U.S. Government Printing Office, Washington 25, D.C. Up-to-date supplementary inserts, which are issued periodically, are available upon request directly from the National Bureau of Standards.*

[2] Standard samples for gases-in-metals, *NBS Tech. News Bull.* **43**, *134 (July 1959).*

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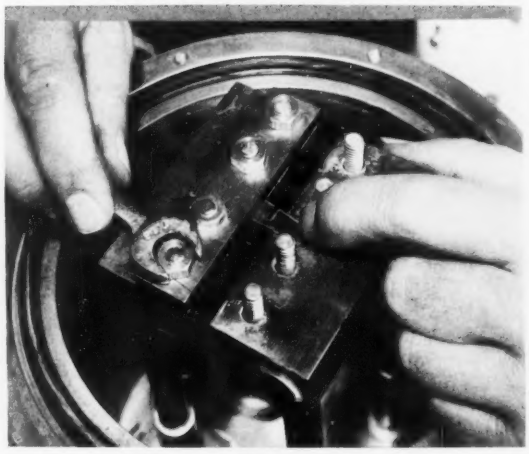
Phase-Equilibrium Studie

A BETTER UNDERSTANDING of the fundamental nature of metal and alloy systems is resulting from research on phase equilibria at the Bureau. In general, these studies are concerned with the effect of varying environmental conditions, such as temperature, pressure, and concentration of components, on the stability and chemical composition of coexisting phases—liquid or solid—in a heterogeneous system.

Each phase in a heterogeneous system is a homogeneous, distinct entity having a certain composition and a particular set of physical properties. In a phase diagram, relations between these various phases are shown by plotting experimental data so that the different phases occupy regions separated in the diagram by lines representing the limiting equilibrium conditions. From such a diagram, useful generalizations may be made regarding other compositions in a given system or those in related systems. The diagram provides a simple, convenient graphical representation of the relationships between mixed or combined elements or compounds such as occur in steel and other alloys. Melting and freezing points and ranges, transformations, solubilities, and reactions which form intermediate phases and intermetallic compounds are depicted. Eventually, it is hoped, the study of phase diagrams may lead to a theory of alloying that can predict behavior for compositions and experimental conditions not yet explored.

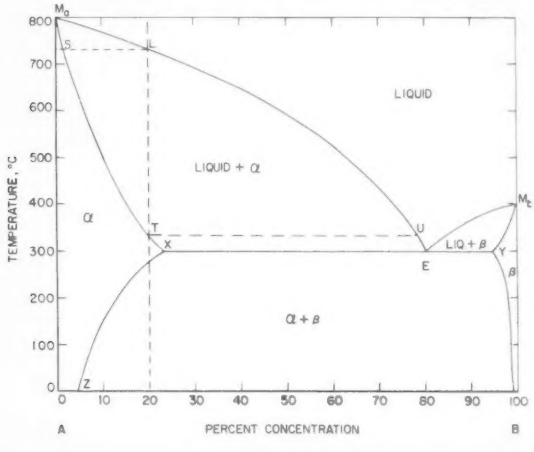
Conventionally, the two-component, or binary, phase-equilibrium diagram consists of a temperature-versus-composition plot. For such a diagram, the temperature is plotted on the vertical axis against the percentage-composition of the two components on the horizontal axis.

Data for these two-component diagrams are obtained from cooling curves recorded in the studies of alloys having various concentrations. Known mixtures are heated to the liquid phase and then gradually cooled while the temperature of the sample is plotted against time. Each time a phase separates out, the cooling curve shows a change in slope because of the heat of reaction. The temperatures at which these changes become evident are then plotted against composition of the alloy.



Notched metal specimen used to determine phases formed at various temperatures. The specimen, held between two water-cooled copper electrodes, is heated by electroresistance as the current passes through it. Sample is quenched by turning off current. With this apparatus, a maximum of at least 2500 °C may be reached. Optical pyrometer is used to measure the temperature of the notched area.

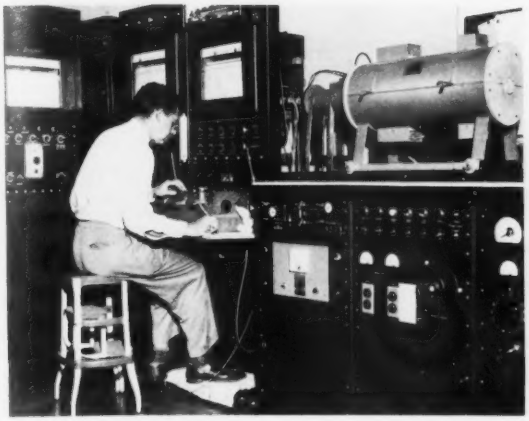
Typical two-component phase-equilibrium diagram.



As an example of a comparatively simple system, the low-melting "binary-eutectic" diagram may be considered (see the typical two-component phase-equilibrium diagram, at left). This diagram depicts the lowering of the melting points, M_a and M_b, of each of the pure metals *A* and *B*, by the addition of the other component, and the subsequent formation of a eutectic with a distinct melting point at *E*. If a particular alloy composition, as for example, that of 20 weight percent (wt %) metal *B*, is cooled down the dashed line from the liquid state to the point *L*, the liquid begins to solidify to form the solid α phase of composition *S*. In this case, in contrast to the freezing of a pure metal, the composition of the first solid is no longer that of the original melt, but rather it is that of point *S*, horizontally to the left of *M;* namely, the solid in equilibrium with liquid *L* at the temperature of *S* and *L*.

Upon additional cooling, the average composition of combined liquid and solid remains 20 percent of *B*, but the liquid's composition changes along the curve *LUE* while the solid's composition follows the curve *STX*. Thus down to the temperature *T*, the solid contains less of *B* than does the original alloy. The liquid

...in Metallurgical Systems



Apparatus for precision measurement of changes of electrical resistance and of dilatation (changes in physical dimensions of metals) at high temperatures. With this equipment, dimensional variations of the order of 10^{-6} in./in. can be measured. G. A. Moore measures furnace temperature during a determination of electrical resistance changes with temperature.

composition gradually increases in content of metal *B*, such that when the mixture finally becomes completely solid at the temperature of *XEY*, the last liquid to freeze has the eutectic composition *E*, and the final composition of phase α is that at point *X*. Similar changes are observed at the other compositions within the system which contain combinations of elements *A* and *B*.

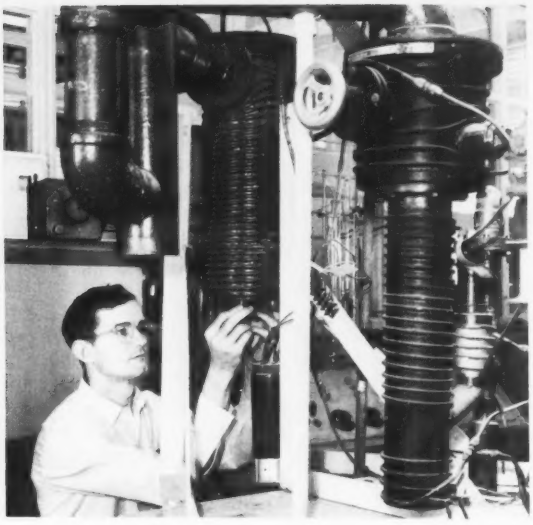
One particular composition, in this case that of 80 percent metal *B*, will exhibit a sharp, distinct, melting point at *E*. This point, called the eutectic point, is the lowest melting combination made up of the elements *A* and *B*. It also is a point on the invariant line *XEY*, the only temperature at which three phases are present in this particular system.

Two other areas of particular interest are the solid solubility regions, α and β. This diagram indicates that over 20 weight percent of metal *B* can be accommodated in the crystal lattice of *A*, provided the temperature is that of line *XEY*. However, when the solid α phase is at equilibrium below this temperature, it can retain less of *B* and will consist of compositions along the curved line *XZ*. The fact that the solid α loses some of metal *B* as the temperature is lowered is of special significance for precipitation-hardening, a phenomenon first explained in 1919 by Merica, Waltenberg, and Scott [1] of NBS. An increase in hardness will occur if an alloy in the field of α is quickly cooled (so that it is not in equilibrium), and is then held at a constant temperature as its equilibrium condition is approached. This hardening, caused by the rejection of the *B*-rich β phase, reaches a maximum after a certain period of time at a specific temperature.

Most phase-equilibrium diagrams are more complex than this diagram, and may include compounds of certain stoichiometric ratios (shown by vertical lines) which may either melt at a definite temperature or which may decompose to a liquid+solid mixture at a particular temperature.

This brief explanation of a simplified two-dimensional phase-equilibrium diagram does not fully emphasize the wide applicability of such diagrams. The construction of a binary-phase diagram is the first step in research to develop modern materials. Not only do these simpler diagrams pave the way for the more complex- ternary and quaternary alloys, but they themselves provide data for both experimental and theoretical research workers. The production metallurgist uses phase diagrams to determine melting points, annealing temperatures, and approximate forging temperatures; the theoretician, on the other hand, may be interested in the stability of particular phases as a function of the electronic structure of the elements or compounds involved.

Zone-melting apparatus in which a metallic rod can be purified of dissolved contaminants. A tungsten heating element bombards the metal with electrons. This action causes progressive, localized melting of a narrow zone in the specimen. During the purification T. R. Shives adjusts remote controls for stretching and rotating the sample, while G. A. Moore (looking through dark glass) checks the position of the end of the rod in the hot furnace.



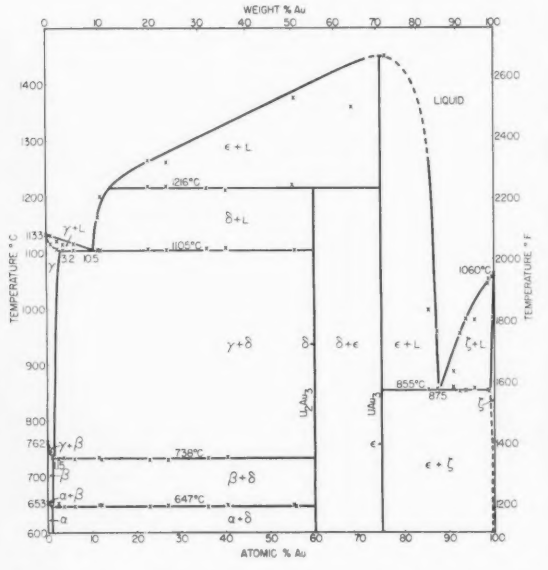
Above, thermal-analysis equipment used to obtain time versus temperature data for phase-diagram studies of metal systems. With the molybdenum-wound resistance furnace, temperatures up to 1400 °C can be achieved. J. J. Park closes furnace in preparation for thermal-analysis run. Below, closeup of thermocouple and crucible arrangement which is inserted into furnace (in photo above). Thermocouple fits into the well in the crucible, which is so designed that the thermocouple tip is surrounded by the metal specimen.

Obtaining the Data

Accurate phase diagrams result from the combination of corroborating data obtained by analyzing high-purity alloys. Thus one important aspect of phase-diagram studies is the development of metals having the highest possible purity. Many of the high-melting metals are difficult to purify and their melting points are generally lowered by impurities. Diagrams plotted from these contaminated metals might not present an accurate picture of the phases occurring in pure metals.

Present equipment at the Bureau provides extremely pure metals, such as tungsten, by a three-step process: (1) chemically purifying a compound of the metal by fractional distillation; (2) decomposing a volatile halide of the metal in a "hot-wire" apparatus to deposit the metal on the hot wire; and (3) melting and refining the wire in a floating-zone apparatus using electron-bombardment heating. Specimens of the fused elements in very high purity can thus be made available for basic research on the metal and on its alloy systems.

The possibility of freeing a metal from a specific impurity by zone refinement can usually be predicted from the phase diagram. For example, it might be desired to separate the metal *A* of the two-component, phase-equilibrium diagram, p. 170, from the impurity *B*. If an original alloy rod had the composition "*L*" and a single drop was melted at one end, the metal which would freeze as the drop was moved along the rod would first be of the much purer composition "*S*." Were this to continue, the liquid drop would soon become so rich in the "*B*" impurity that no further puri-



Binary phase diagram showing reactions between gold and uranium. This diagram indicates the presence of 2 eutectics and 2 compounds.

Right, D. P. Fickle adjusts heat shield for thermal-analysis furnace. This shield can be attached to a furnace for quenching at a desired temperature.

fication would occur. However, if the original metal was nearly "chemically pure," that is, had much less *B* in it, a useful length of rod could be effectively treated by passing the molten zone along the rod many times, whereby more and more of the impurity *B* could be rejected until finally metal *A* had a purity in the parts per million range, or even in some cases, impurities measured in parts per billion.

Once a series of alloys is prepared from the component metals, conventional methods of thermal analysis and microscopy are employed to obtain most of the data for phase diagrams. However, because no one procedure can supply all the data needed, many test methods are employed to examine such structure-sensitive properties as magnetic susceptibility, hardness, and internal friction. In addition, dilatation measurements may be obtained over a range of temperatures, and measurements of electrical resistance versus temperature (resistometric measurements) may be recorded. X-ray and other diffraction techniques serve to identify various phases, to determine the ordering of atomic structures, and to establish solubility limits.

Thermal analysis involves the continuous measurement or recording of the temperature of the specimen as it is heated or cooled under carefully controlled conditions. Differential thermal analysis, a more sophisticated method, determines the temperature of an experimental alloy in comparison with a neutral control substance—that is, one which has no expected changes over the temperature range under study. Any reaction in the experimental alloy will be revealed as a temperature difference between it and the reference standard. Comparable results should be obtained by the two thermal analysis systems, although the metallurgist selects that particular technique best suited for detecting the specific reaction of immediate concern.

Microscopy—particularly light microscopy—was the first, and is still the most useful, technique for determining phase changes, limits of solubility, and type of reaction. In the light microscopy of such opaque materials as metals, the light is reflected from a polished and etched section of a specimen. This procedure reveals a great deal about the microstructure of the specimen. In general, the topological information revealed by the microscope has been qualitatively interpreted by the metallographer in terms of his experience. However, through recent Bureau research,[2] the micrographs can now be directly scanned by high-speed computers which provide a quantitative analysis of the microstructural information. For studying more minute structural changes, the electron microscope is employed; this instrument may detect elements of structure in the range of 10 Angstrom units (10×10^{-8} cm).

Below, H. Yakowitz views specimen in electronprobe microanalyzer. The composition of microconstituents in a metallurgical specimen can be determined by analyzing the characteristic X-rays emitted from a small spot about 1 μ in diameter.

A further advance in this field is the electronprobe microanalyzer, which enables determination of the composition of individual grains, precipitated phases, and inclusions *in situ* as composition gradients across diffusion zones. The composition is obtained by analyzing the characteristic X-rays emitted from a small area about 1 μ in diameter—the diameter of the electron beam creating the X-ray excitation. The finely focused electron beam is generated by an electron optical system similar to that in an electron microscope. A light optical microscope is centered on the axis of the electron optical system for viewing the microstructure and positioning the area of interest under the electron beam.

In addition to its use as an auxiliary instrument for obtaining the composition of specific phases, the electronprobe microanalyzer is particularly useful as a primary instrument for determining phase-equilibrium areas in the solid-state portion of the diagrams, where the sluggishness of the alloy transitions often seriously limits the precision of thermal-analysis methods. Equilibrium-phase boundaries can be located directly from composition-gradient curves which are obtained with the electronprobe from diffusion-couple specimens. These are specimens that have been held at selected temperatures in separate furnaces to develop the complete sequence of phases that will occur between the two pure metals at the respective temperatures. Data on the kinetics of the reaction which are not generally determined by thermal-analysis techniques are obtained by the electronprobe procedure.

R. J. Snodgrass positions a dewar flask containing a metal specimen into the probe of a nuclear-magnetic-resonance spectrometer set between the pole caps of a large electromagnet. Liquid nitrogen in the dewar permits resonance studies to be made at −196 °C without affecting the probe temperature.

Nuclear magnetic resonance has proved an effective tool for revealing aspects of the electronic structure of alloys on which, in part, their phase constitution must depend. The resonance technique utilizes the atomic nucleus as a probe to measure magnetic and electric fields inside the metal. Detailed analysis of these fields furnishes data on the electronic densities in the metals and relaxation mechanisms, as well as the effects of impurities, imperfections, and atomic ordering. Determination of the electronic structure of the system, i.e., the allowed energy states available to electrons in alloys, can frequently lead to an understanding of alloying behavior and not merely to a description of it. Metals, alloys, and intermetallic compounds containing nickel, lead, indium, tantalum, niobium, and cobalt are presently being studied.

Studies of Binary Systems

Current NBS studies of phase relationships cover numerous systems ranging from high-temperature metals and alloys to dental amalgams. As part of this program, systematic studies of the binary-phase relationships between uranium and related groups of elements are being conducted in the Metallurgy Division. This study is being sponsored by the Atomic Energy Commission. Previous investigations to provide information on the alloying behavior of uranium have dealt with reactions between uranium and beryllium,[3] silver,[4] gold,[5] and platinum,[6] respectively. Although silver, gold, and copper appear in the same group of the periodic chart, their phase diagrams show that the compounds they form with uranium and the shapes of the liquidus curves are far from identical. Thus, although the copper-silver-gold series might be expected to react similarly with uranium, the equilibrium diagrams show that one compound occurs in the U-Cu system, none in the U-Ag system, and two in the U-Au system.

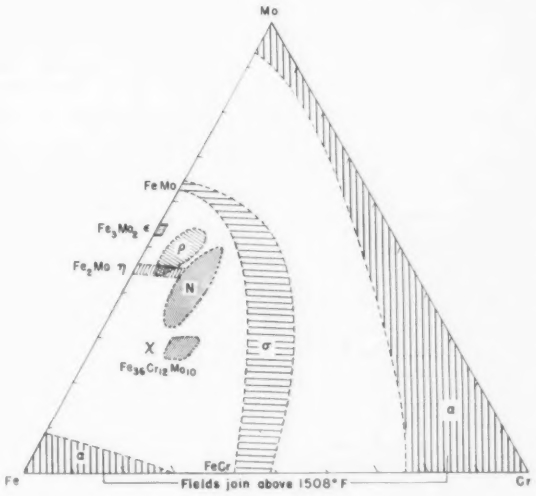
Present work involves studies of the reactions of uranium with the individual platinide metals and with rhenium. Four compounds were found within the U-Pt system. Although the platinide elements have many similarities, platinum can dissolve only 4.5 atomic percent uranium, whereas present studies indicate that palladium dissolves at least 15 atomic percent uranium. It is necessary to know the reactions of uranium with the platinide metals because ruthenium, rhodium, and palladium are produced in significant amounts during the fissioning of uranium in a nuclear reactor and so must be removed when refining the

uranium. Furthermore, the reactions of the platinide metals with uranium are greatly dependent upon the properties peculiar to each, although these elements are in the same group of the periodic chart.

The work with uranium and related metals has been accelerated by development of equipment that is especially applicable to high-temperature studies. One instrument utilizes the electrical resistance of a specimen so that it may be heated to 2500 °C and above when an electric current passes through it. Quenching of the specimen, which is held between water-cooled electrodes, is quickly accomplished by turning off the current. This device has the advantage of operating without a ceramic crucible, thus avoiding the undesirable alloy-crucible reaction which is extremely common when conventional apparatus is used at high temperatures.

To study alloy reactions at temperatures up to 1400 °C, a fully automated thermal-analysis furnace has been constructed. This furnace has a controlled heating and cooling rate which may be set at rates between 1 and 5 °C per minute and can be operated either under a vacuum or with an inert atmosphere. The apparatus was modified to permit quenching a specimen in oil after the test material has been slowly heated or cooled to a temperature near a phase reaction.

In the semiconductor field, the Bureau has investigated congruous-melting intermetallic compounds formed between Group III and Group V elements of the periodic chart, such as indium antimonide (InSb).

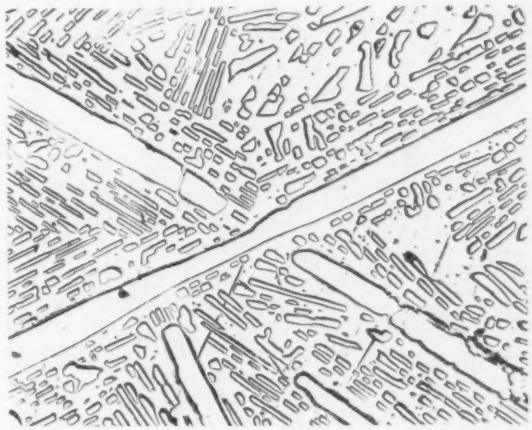


Schematic representation of compositions of intermetallic compounds formed in the ternary chromium-iron-molybdenum system. This phase diagram covers the temperature range from liquidus to room temperature. The overlapping of the rho (ρ) and eta (η) fields indicates a solid-state transition at about 950 °C (1750 °F).

The increasing industrial use of semiconducting devices such as rectifiers and transistors, along with the present interest in employing semiconductors as infrared photodetectors and thermoelectric generators, emphasizes the need for a better understanding of the unusual mechanical and electrical properties of these solids. The intermetallic compound, InSb, has been studied in relation to other group III–V compounds such as indium arsenide (InAs). It has also been examined for phase and structural relationships in the pseudo-binary system between these intermetallic compounds. Interestingly, both the In-Sb system and the In-As system exhibit only the one compound, having the 1:1 atomic ratio, with a eutectic on each side of the compound.

A better understanding of the mercury-silver-tin system—the basis of the silver-alloy system used to restore teeth—and of the reactions that occur in the hardening of dental amalgam is of immediate importance to dentistry and may lead to applications in other alloy systems as well. Dental amalgams are made by mechanically mixing a finely divided, solid silver-tin alloy with the liquid mercury. The hardening process then proceeds by isothermal diffusion and by the reaction of the components. It is of interest to note that, in this example of alloy formation with mercury as the solute metal, the same kinds of metallurgical reactions occur at room temperature that require a temperature of nearly 2000 °C for such systems as the uranium alloys.

The Bureau's dental research staff is now studying the binary tin-mercury alloys to obtain the data required to complete the phase diagrams for this system. In general, experiments so far have indicated that the system is more complicated than previously believed. Results indicate the existence of at least two new phases.



Photomicrograph of uranium-17.7 atomic percent platinum alloy showing U-Pt phase in α-uranium matrix. Approximately 40X. The systematic investigation of uranium with related groups of elements is part of a Bureau study on phase equilibria.

Other phase-equilibrium investigations have dealt with materials for highly stable gage blocks. The Bureau now calibrates industrial master gage blocks, which are used as standards for controlling the accuracy of mass-produced machine parts, to an accuracy of 1 ppm (part per million). In special cases, it has even been possible to certify gage blocks to an accuracy of better than 1 part in 5 million. To improve the accuracy of gage blocks even more, suitable alloys for preparing such ultra-precise gage blocks must be selected. These materials must have sufficient hardness to resist wear, and a high degree of dimensional stability. Through phase-relationship experiments, a nitrided stainless steel was found to have excellent dimensional stability characteristics and is now being investigated further.[7]

Studies on the pyrometallurgical recovery of uranium from spent fuel elements are being conducted for the Atomic Energy Commission. Economically, the removal of the fission-product elements and the recovery and re-use of the uranium are significant factors in the nuclear energy program.

Potential recovery processes involve the differential solution of uranium and fission products in liquid metals. In these studies the lack of accurate phase-diagram information has made necessary the initiation of several binary-diagram investigations. Because uranium fission produces a relatively large amount of ruthenium, the study of the ruthenium-zinc system has been undertaken. One compound—$RuZn_9$—has been observed. This compound could cause undesirable side effects in a recovery process utilizing zinc.

Phase-diagram studies have furnished basic information on the many reactions occurring between the components and constituents of metal systems. The present trend in this area is toward an understanding of the forces involved in alloying reactions and the effects produced upon the atom by the addition of another element. A soft X-ray spectrometer is being designed to study the distribution of occupied electron-energy levels, thereby providing valuable information on bonding in metals.

Ternary and Higher Systems

Although the binary system is the basic building block for most alloys, ternary or higher diagrams are more frequently employed. For example, in an investigation sponsored by the Navy Bureau of Ships, ternary studies were utilized to improve the corrosion resistance of the original binary alloy of 60 weight percent chromium and 40 weight percent nickel. This binary alloy appears to be highly resistant to the environmental condition in oil-fired Navy boilers. Ternary alloys based on Cr–Ni were prepared with a different metal as the third component. Results indicated that small amounts of titanium, yttrium, or magnesium increase the chromium-nickel alloy's resistance to the experimental corrodents which were employed.

Another ternary study is now being conducted on stainless steels. Unknown variables were found to cause erratic performance of one of the stainless steels frequently used for aircraft components. In order to identify these variables, a program is under way to establish the constitution diagram for high-purity alloys and steels containing various chromium-nickel ratios. This study has been extended to quaternary alloys composed of iron, chromium, nickel, and molybdenum, in which the ratios of certain components are held constant while the others are varied. It is hoped that information will be obtained on the mechanism of formation of the "sigma" phase, a compound of characteristic structure—and usually of deleterious nature—found in stainless steels and many other alloys.

Some data have been obtained by progressing from the binary iron-chromium system and other binary systems to the ternary systems involved and, in turn, to the quaternary iron-chromium-nickel-molybdenum system. For example, examination of the chromium-nickel system [8] has revealed the existence of a previously unreported phase of the beta-manganese type. In addition, a new phase believed to have the composition MoNi has been discovered in the molybdenum-nickel system, and a phase of the Fe_7Mo_6(Fe_3Mo_2) type has been found in the chromium-molybdenum-nickel system.

Although much useful information has resulted from phase-equilibrium studies, a great deal more research remains to be done in this field. Thus far, from a potential of more than 5000 binary systems of metallurgical interest, scarcely 900 have been investigated, and a much greater number of higher-order systems are still to be studied. The Bureau plans to continue and intensify its efforts to fill some of the gaps in our present knowledge of metallurgical systems.

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[1] Heat treatment of duralumin *by P. D. Merica, R. G. Waltenberg, and H. Scott, Bull. Am. Inst. Mining Eng. No.* **150,** *913 (1919).*

[2] Quantitative Metallography, *G. A. Moore, L. L. Wyman, and H. M. Joseph, McGraw Hill, to be published.*

[3] Beryllium-uranium system, *R. W. Buzzard, J. Research NBS* **50,** *63 (1953) RP2389.*

[4] Silver-uranium system, *R. W. Buzzard, D. P. Fickle, and J. J. Park, J. Research NBS* **52,** *149 (1954) RP2483.*

[5] The gold-uranium system, *R. W. Buzzard and J. J. Park, J. Research NBS* **53,** *291 (1954) RP2547.*

[6] Uranium-platinum system, *J. J. Park and D. P. Fickle, J. Research NBS* **64A** *(Physics and Chemistry) 107 (1960); NBS Tech. News Bull.* **44,** *57 (1960).*

[7] Extremely stable gage blocks for precision measurements, *NBS Tech. News Bull.* **44,** *82 (1960).*

[8] Redetermination of the chromium and nickel solvuses in the chromium-nickel system, *C. J. Bechtoldt and H. C. Vacher, Trans. of Metallurgical Society, AIME,* **221,** *14 (1961).*

Low-Level Carbonate Determination by Gas Phase Chromatography

A SIMPLE AND RAPID gas phase chromatographic procedure for the determination of carbonate at low levels [1] has been developed by F. G. Carpenter [2] of the surface chemistry laboratory. The method, which involves evolution of carbon dioxide with acid, is normally used to determine the carbonate content of solids or liquids. It has a detection limit of 0.2 part per million, and an uncertainty of less than one percent.

Using standard gravimetric or volumetric techniques—and retaining a reasonable sample size—amounts of carbonate below 10 parts per million are difficult to measure without sacrificing speed and ease of manipulation. The use of gas phase chromatography for measurement of carbon dioxide has made it possible to extend the rapid analysis of carbonate by another order of magnitude.

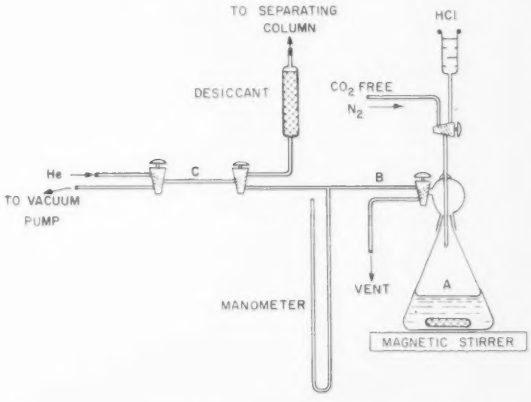
In the chromatographic procedure, solutions of known volume or samples of known weight are placed in a 125-ml flask which is attached to the analytical apparatus. The flask is swept with CO_2-free nitrogen, and evacuated to ½ atm. Ten milliliters of 3N HCl are drawn into the flask, and the sample-acid mixture is stirred vigorously—with a magnetic stirrer—for 5 min. A 10 ml portion of the gas is withdrawn for analysis.

This gas sample is swept with helium to the chromatographic column, passing first through a very small tube of magnesium perchlorate to remove the water vapor present. The water-free gas then passes through a 30-cm-long column packed with silica gel at a flow rate of 4 cm/s. The gases leaving the separation column are analyzed with a thermal conductivity detector, the output of which is recorded on a strip chart. Analyses made with this system can be completed in 10 min or less.

The apparatus must be calibrated with pure CO_2 prior to use, as the technique does not provide an absolute measure of carbonate content. At the Bureau the method was checked by analysis of both NBS Standard Limestone and a standard solution of sodium carbonate. Good agreement was obtained in each case.

[1] *For further details, see* Use of gas phase chromatography for rapid determination of carbonate at low levels, *by F. G. Carpenter, Anal. Chem. (to be pub.).*

[2] *Research associate at the National Bureau of Standards representing Bone Char Research Project, Inc.*



Apparatus used to generate and dry CO_2 prior to separation in a silica gel column. HCl is added to the sample in the flask (far right) and the mixture is stirred for 5 minutes. The gas from the flask is then released to fill *B* and *C*. The 10 ml portion of gas in *C* (total *A*, *B*, and *C* is 160 ml) is swept with helium through a magnesium perchlorate tube to remove water, and then passes to the separation column. A thermal-conductivity detector is used to determine the amount of CO_2 present.

H. M. Rootare admits acid to the sample-containing flask to liberate CO_2. A portion of the gas, after passing through a water-removing column, will be separated in a silica gel column, then passed through a thermal-conductivity detector.

Effect of Dodecyl Alcohol on Fatigue Crack Propagation

THE RATE of fatigue crack propagation through a metal specimen is significantly reduced by the presence of an organic liquid such as dodecyl alcohol on the test section, according to a recent Bureau study. This finding was made in one of a series of studies sponsored by the National Aeronautics and Space Administration to investigate the role played by surface reactions in fatigue failure, a phenomenon that may occur in any material subjected to alternating stresses. The study was conducted by W. L. Holshouser and H. P. Utech of the mechanical metallurgy laboratories.[1]

Fatigue failures are progressive and consist of two phases, the first, crack initiation, extending from the start of the stress application to the appearance of the first crack (which ultimately causes specimen failure); the other, a period of crack propagation, which terminates with the abrupt fracture of the piece. In a laboratory test the duration of each phase depends on the type of specimen used. In earlier Bureau work [2] with smooth cylindrical specimens, it was found that the presence of certain polar organic liquids on the surface of the specimens increased the fatigue strength of several metals. This improvement was primarily a measure of the effect of the liquids on fatigue crack initiation, since a large portion of the total life of the specimens had been expended before cracks appeared. The reason for the improvement was thought to be that the polar compounds formed films on the metal which prevented deleterious reactions between the metal and the atmosphere.

H. P. Utech adjusts apparatus used to apply dodecyl alcohol to the notched area of a specimen. The specimen is mounted in the spindles of a rotating-beam fatigue-testing machine.

To obtain information on the effect of such compounds on the crack propagation phase, fatigue tests were conducted with sharply notched cylindrical specimens in both a clean condition and with dodecyl alcohol on the surface. The notches serve as stress raisers; as a result, the effective stress at the root of the notch greatly exceeds the nominal stress applied to the specimen, and cracks appear at the notch at an early stage of fatigue life.

In the study, tests were conducted on specimens of 4340 steel, 17–7 PH stainless steel, 6061 aluminum alloy, and a copper-beryllium alloy (1.75 percent Be). They were 0.365 in. in diameter, and notched around the middle to a reduced diameter of 0.250 in. To prevent variations in surface finish and in the amount of cold work produced in the surface of a specimen, the 0.005-in. radius at the root of each notch was carefully ground. All of the tests were run on rotating-beam machines of the R. R. Moore type, operated at 3000 rpm.

To determine the approximate point in the fatigue life when cracks first appeared, fatigue specimens of each metal were tested for small percentages of their expected fatigue life, and longitudinal sections of the specimens were examined metallographically for cracks. An analysis showed that the approximate portion of total fatigue life expended before cracks appeared was 5 percent for the steel and aluminum; 10 percent for the copper-beryllium alloy; and 35 percent for the stainless steel.

Specimens to be tested in the coated condition were first stressed in the clean condition for the duration of their crack initiation period, and then for the remainder of the fatigue life, dodecyl alcohol was dripped into the notch. The results of these tests are given in the table. Data for all four alloys show that the duration of the crack-propagation period at two stress levels was increased by the dodecyl alcohol coating.

The results indicate that the coating, by limiting the access of molecules of oxygen or water to the metal surface, reduces the rate of detrimental surface reactions that normally occur when specimens are stressed in air. Two materials, the aluminum and stainless steel, showed a greater beneficial effect with notched specimens than they did with smooth specimens in the earlier study. This result may be associated with the relatively impermeable and adherent oxide films that form on these metals. Prior to crack initiation, these films apparently minimize detrimental surface reactions. During the crack-propagation phase,

Results of tests to determine the effect of dodecyl alcohol on faitgue crack propagation

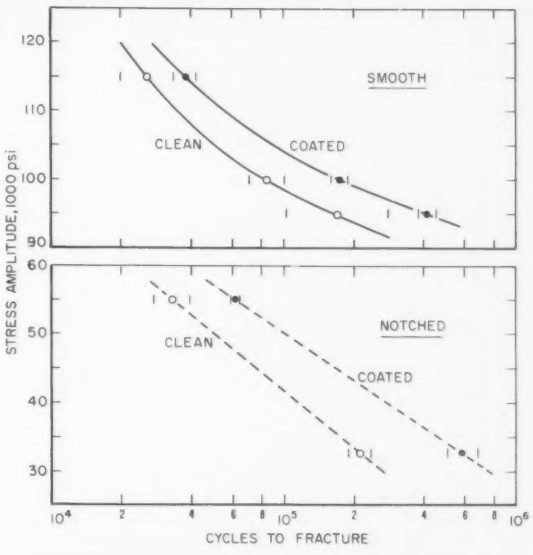
Material	Nominal stress amplitude (1000 psi)	Thousands of cycles of stress						Ratio of Np values coated/clean
		Clean			Coated with dodecyl alcohol			
		Nf [a]	Nc [b]	Np [c]	Nf [a]	Nc [b]	Np [c]	
4340 steel	32.5	210	10	200	586	10	576	2.9
	55	33	2	31	63	2	61	2.0
Cu-Be	30	749	78	671	3406	78	3328	5.0
	50	27	3	24	39	3	36	1.5
6061-T6 aluminum alloy	11.5	358	18	340	632	18	614	1.8
	17	81	4	77	120	4	116	1.5
17-7 PH stainless steel	42.5	115	40	75	325	40	285	3.8
	52.5	32	12	20	39	12	27	1.4

[a] Median fatigue life (5 to 7 specimens).
[b] Number of cycles required to produce a detectable crack.
[c] Nf-Nc (crack propagation portion of fatigue life).

however, each increment of crack extension provides an area of clean metal surface that may react with any oxygen in the atmosphere.

While these considerations provide a possible explanation for the effects of dodecyl alcohol coatings on crack initiation and propagation, the mechanism of the effect of surface reactions on fatigue is still not clear. Recent work, both at the Bureau and elsewhere, tends to show that the oxygen and the water vapor in the atmosphere are responsible for the reduction in fatigue life. Nevertheless, little explanation can be offered as to the manner in which these components accomplish the reduction until more is known about the entire fatigue process.

S–N curves obtained in studies of metal fatigue on both smooth and notched specimens of 4340 steel.



[1] *For further technical details, see* Effect of oleophobic films on fatigue crack propagation, *by W. L. Holshouser and H. P. Utech, Trans. ASTM, Preprint No. 72 (1961).*

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